

# X-ray Investigation of the Magneto-elastic Instability of $\alpha'$ - $\text{NaV}_2\text{O}_5$

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We present an X-ray diffuse scattering study of the pretransitional structural fluctuations of the magneto-elastic transition in  $\alpha'$ - $\text{NaV}_2\text{O}_5$ . This transition is characterized by the appearance below  $T_{sp} \sim 35\text{K}$  of satellite reflections at the reduced wave vector  $(1/2, 1/2, 1/4)$ . A large regime of structural fluctuations is measured up to 90 K. These fluctuations are three dimensional between  $T_{sp}$  and  $\sim 50\text{K}$  and quasi-one dimensional above  $\sim 60\text{K}$ . At 40 K the anisotropy ratio ( $\xi_b : \xi_a : \xi_c$ ) is found to be  $(3.8 : 1.8 : 1)$ , which reveals the importance of transverse interactions in the stabilization of the low temperature phase. We discuss our results within the framework of recent theories dealing with the simultaneous occurrence of a charge ordering, a spin gap and a lattice distortion in this intriguing compound.

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First observed in the 70's in the organic compounds  $\text{MEM}(\text{TCNQ})_2$  [1] and  $\text{TTF-CuBDT}$  [2], [3] and later in the charge transfer salts  $(\text{TMTTF})_2\text{PF}_6$  [4],  $(\text{TMTTF})_2\text{AsF}_6$  [5] and  $(\text{BCP-TTF})_2\text{X}$  [6], [7] (where  $\text{X}=\text{PF}_6$  and  $\text{AsF}_6$ ), the spin-Peierls (SP) transition regained interest after its discovery in the inorganic system  $\text{CuGeO}_3$  [8]. The SP ground state is a magneto-elastic distortion of a one-dimensional (1D) antiferromagnetic chain of spin-1/2. Below the transition temperature  $T_c$  a singlet-triplet gap opens in the magnetic excitation spectrum, accompanied by a lattice doubling of the chain. Theoretically, the SP transition is driven by one-dimensional antiferromagnetic fluctuations coupled to the lattice via the spin-phonon coupling. Accordingly, a strong and anisotropic regime of lattice fluctuations is expected to occur. Nevertheless, SP systems do not all exhibit such a regime of fluctuations as we already emphasized in a previous study [9]. In  $\text{MEM}(\text{TCNQ})_2$  and  $\text{TTF-CuBDT}$  the temperature dependence of the magnetic susceptibility  $\chi(T)$  down to  $T_c$  is well accounted for by a Bonner-Fisher (BF) law of a one-dimensional  $S=1/2$  Heisenberg chain. However, an isotropic x-ray diffuse scattering at the location of the low temperature superlattice reflection remains until high temperature [9] [3]. On the other hand, in  $(\text{BCP-TTF})_2\text{AsF}_6$  a quasi-one dimensional fluctuation regime is observed and  $\chi(T)$  exhibits a sizeable deviation from the BF law, interpreted as due to the influence of the lattice fluctuations on the spin degrees of freedom [10]. As far as  $\text{CuGeO}_3$  is concerned, an anisotropic fluctuation regime has been observed until  $\sim 2.5T_c$  [11]. Here again,  $\chi(T)$  does not follow the BF law due to either deviation from one-dimensionality or to the presence of sizeable next-nearest neighbor interactions. All these results show that, although the spin-Peierls transition concept was successfully used to describe all these magneto-elastic transitions, the experimental situation is much more intricate.

The inorganic compound  $\alpha'$ - $\text{NaV}_2\text{O}_5$  has recently been shown to undergo a magneto-elastic phase transition at  $T_c = 34\text{K}$  [12]. Above  $T_c$ ,  $\chi(T)$  follows remarkably the BF law (with the exchange constant  $J/k_B = 280\text{K}$ ) and the abrupt decrease of  $\chi(T)$  below  $T_c$  is accompanied by a lattice doubling observed by x-ray diffraction [13]. Moreover, the existence of a spin gap  $\Delta$  of  $\sim 10\text{meV}$  was evidenced by inelastic neutron scattering carried out on a powder sample [13]. These observations suggested that  $\alpha'$ - $\text{NaV}_2\text{O}_5$  might undergo an "ideal" SP transition, suitable to test more precisely the current theory of 1D quantum spin systems. The orthorhombic structure ( $a=11.311\text{Å}$ ,  $b=3.61\text{Å}$  and  $c=4.80\text{Å}$ ) consists of double-rows of edge-sharing  $\text{VO}_5$  pyramids running in the **b** direction, and oriented alternately upward and downward in the **a** direction. These (**a**,**b**) layers are separated by  $\text{Na}^+$  cations in the **c** direction. The first description of the structure [14] used the non-centrosymmetric space group  $P2_1mn$ , which described the compound as an assembly of alternating magnetic  $\text{V}^{4+}$  ( $S=1/2$ ) and non-magnetic  $\text{V}^{5+}$  ( $S=0$ ) chains. However, careful reinvestigations of the structure [15], [16], have shown that the actual space group is the centrosymmetric one,  $Pm\bar{m}n$ , which implies that all the V-chains are equivalent. The same conclusion was drawn from  $^{51}\text{V}$  NMR measurements [17]. Only one set of V sites is found in the spectrum above  $T_c$ , while two inequivalent sets of V sites, assigned to  $\text{V}^{4+}$  and  $\text{V}^{5+}$ , are observed below the transition, evidencing a charge ordering process associated with the phase transition. These observations have made more difficult the description of the compound as made of an assembly of spin-1/2 chains. Furthermore, in contrast with other SP systems where the spin gap has been measured, the ratio  $2\Delta/kT_c$  is equal to 6.5 instead of the BCS-value 3.52. Additional thermodynamic measurements [18] have also indicated the occurrence of two phase transitions very close to  $T_c$ , one of them being first-

order.

All these results show that  $\alpha'$ - $\text{NaV}_2\text{O}_5$  undergoes a magneto-elastic transition far to be correctly described by the conventional spin-Peierls scenario. Especially interesting is the concomitant occurrence (in the experimental limits given in ref. [18]) of a charge ordering, a spin gap and a lattice doubling. Theoretical studies have recently addressed this issue [16] [19] [21] [22] [20]. An attractive model considers the system as a quarter-filled ladder compound [19] [16] [21] [22]. By taking into account the on-site and intersite Coulomb interactions, different types of charge ordering are considered. In the 'chain' model, the  $\text{V}^{4+}$  are ordered along one leg of the ladder but a conventional spin-Peierls mechanism is still invoked to stabilize the lattice distortion leading to the spin gap [21] [20]. In a second model in which the  $\text{V}^{4+}$  form a 'zig-zag' pattern along the ladder, the spin gap is seen as a natural consequence of the transverse order, although the exact mechanism of the spin pairing is controversial [19] [22]. As far as the lattice coupling is concerned, Mostovoy *et al* [22] emphasized its importance in stabilizing the 'zig-zag' ordering with respect to the 'chain' one. Besides, the role of the transverse interactions has not been investigated in detail in these studies. In order to clarify these points, we have performed an x-ray study of the pretransitional structural fluctuations of  $\alpha'$ - $\text{NaV}_2\text{O}_5$ .

Crystal growth was carried out by the flux method by melting under vacuum in platinum crucibles appropriately compacted mixtures of  $\text{V}_2\text{O}_5$ ,  $\text{V}_2\text{O}_3$  and  $\text{NaVO}_5$ . These melts were then slowly cooled from 1073 K to room temperature. Depending on the cooling rate, either needle-shaped or plated-shaped crystals were obtained. In this study, needle-shaped single crystals were used. A preliminary x-ray photographic study with Cu  $K\alpha$  radiation first confirmed the appearance of satellite reflections below  $T_{sp} = 35$  K at the reciprocal positions  $(h + \frac{1}{2})\mathbf{a}^* + (k + \frac{1}{2})\mathbf{b}^* + (l \pm \frac{1}{4})\mathbf{c}^* \equiv \mathbf{G}_{hkl} \pm \mathbf{q}$ . These new spots were found to be more intense at large angles and low  $k$ . Attempts to observe diffuse scattering above the phase transition failed however, mainly because of a large background due to the Cu  $K\alpha$ -induced fluorescence of vanadium. A long crystal ( $\sim 9 \times 0.3 \times 0.2$  mm<sup>3</sup>) was then attached on the cold stage of a closed-cycle He refrigerator installed on a normal beam-lifting-detector diffractometer. The x-ray measurements were performed using monochromatic Mo  $K\alpha$  radiation. The low temperature (30 K) lattice parameters were found to be  $a=11.3$  Å,  $b=3.6$  Å and  $c=4.75$  Å, in agreement with ref. [12]. The experimental resolution given by the Half-Width at Half-Maximum of the intense  $(-1.5, 0.5, -2.75)$  satellite reflection at 30 K was  $R_a = 0.02$  Å<sup>-1</sup>,  $R_b = 0.04$  Å<sup>-1</sup>,  $R_c = 0.04$  Å<sup>-1</sup>. As shown in the inserts on figure 1, the profiles were best fitted by a sum of two Gaussian lines, indicating the presence of multiple components in the crystal.

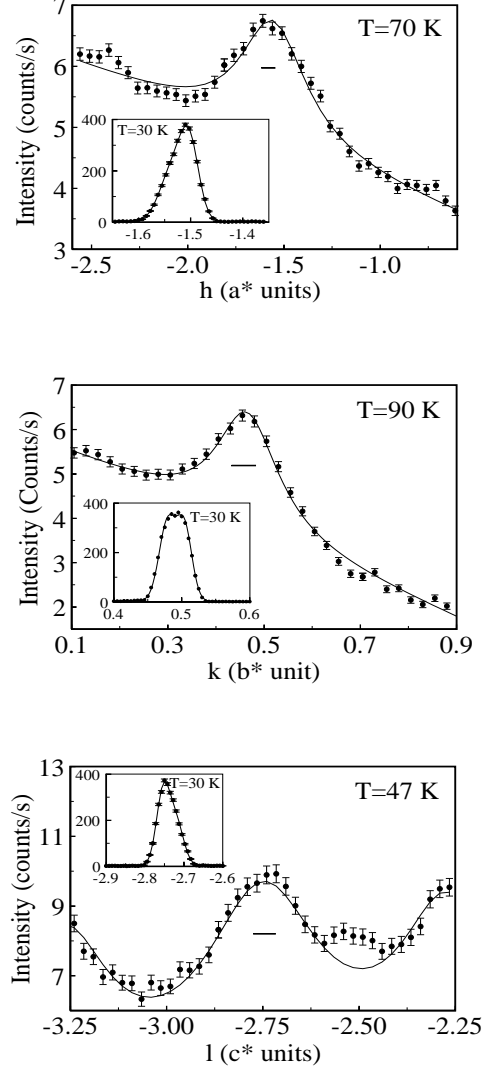


FIG. 1. Scans of the  $(-1.5, 0.5, -2.75)$  peak at 70 K, 90 K and 47 K in the  $\mathbf{a}^*$  (top),  $\mathbf{b}^*$  (middle) and  $\mathbf{c}^*$  (bottom) directions respectively. The inserts show the same scans at 30 K. The solid lines are the results of the fits described in the text. The lines under the peaks indicate the experimental resolution  $2R$  (see text).

We have measured the temperature dependence of the scattering around the reciprocal position  $(-1.5, 0.5, -2.75)$  from 30 K to 90 K by scanning in the three directions of the reciprocal space. The peak intensity  $I$  was obtained from the  $\mathbf{b}^*$ -scans by subtracting the background intensity. Figure 2 displays the temperature dependence of  $I$ , proportional to the square of the structural order parameter, together with the behavior of  $T/I$ , proportional to the inverse of the susceptibility associated with this order parameter. Both quantities vanish continuously at  $T_{sp}$ , consistently with a second-order phase transition. Yet, below  $T_{sp}$ ,  $I(T)$  is fitted by the power law  $(T - T_{sp})^{0.3}$ , which leads to a critical ex-

ponent  $\beta \sim 0.15$ . Although this value could correspond to an artifact due to resolution effects close to  $T_{sp}$ , it is noteworthy that a similar fit, using the synchrotron data of Fujii *et al* [13] in the same temperature range, gives an exponent of  $\beta \sim 0.2$ , sizeably different from the mean-field value 0.5 or the 0.35 exponent expected for the behavior of an XY 3D order parameter. Interestingly, a similar value ( $\beta = 0.25$ ) was extracted from infrared reflectivity measurements [23]. As shown on figure 2, the behavior of  $T/I$  is also unusual and exhibits a crossover at  $\sim 50$  K instead of a Curie law.

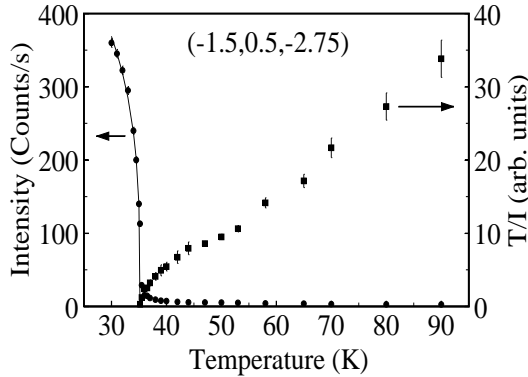


FIG. 2. Thermal variations of the intensity  $I$  of the  $(-1.5, 0.5, -2.75)$  peak (right scale) and of  $T/I$  (left scale). The solid line is a fit by the power law  $(T_{sp} - T)^{0.3}$ .

Above  $T_{sp}$ , the intrinsic correlation lengths (fig. 3) were obtained by a deconvolution procedure, consisting in fitting the measured line shapes by the one-dimensional convolution of the resolution function, obtained at low temperature, and a parametrized function that we chose to be a Lorentzian. This procedure is known to give good results except close to  $T_{sp}$ , where the influence of the other directions becomes essential. Figure 1 shows typical scans of the  $(-1.5, 0.5, -2.75)$  peak at 70 K, 90 K and 47 K in the  $\mathbf{a}^*$ ,  $\mathbf{b}^*$  and  $\mathbf{c}^*$  directions respectively. Due to the  $1/4$  value of the reduced wave vector in the  $\mathbf{c}^*$  direction, the proximity of the peaks did not allow us to fit the scans in this direction at temperatures larger than 47 K. A similar problem of background subtraction occurred above 70 K in the  $\mathbf{a}^*$  direction. As shown in figure 1, a peak is still clearly visible at 90 K ( $\sim 2.5T_{sp}$ ) in the  $\mathbf{b}^*$  direction, indicating a very large domain of structural fluctuations. We will define a dimensional crossover as usual when a correlation length reaches the average distance between basic units in one direction. Within this definition, a 3D to 2D crossover takes place at  $\sim 50$  K, where the extrapolated value of  $\xi_c$  reaches  $c=3.6$  Å. Because of the complex structure of  $\alpha'$ - $\text{NaV}_2\text{O}_5$  the actual distance between the double-rows (or ladders) in the  $\mathbf{a}$  direction is  $a/2 = 5.65$  Å. This leads us to consider the system as quasi-1D above  $\sim 60$  K. It is noteworthy that  $\xi_b = 7.7$  Å at 90 K, which corresponds

to twice the distance between V atoms in the chain direction. At 40 K the anisotropy ratio ( $\xi_b : \xi_a : \xi_c$ ) is equal to  $(3.8 : 1.8 : 1)$ , in qualitative agreement with the structural anisotropy of the compound.

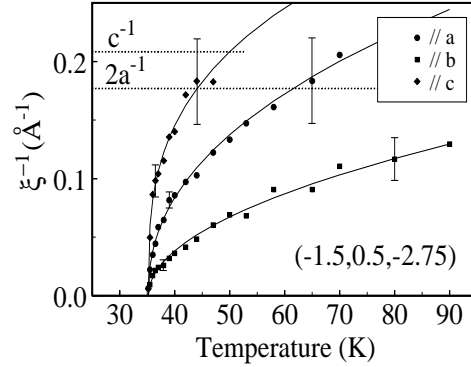


FIG. 3. Thermal variations of the inverse of the correlation lengths in the  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$  directions. The solid lines are guides for the eyes. The dashed lines indicate the inverse values of  $c$  and  $a/2$ .

First of all, in the absence of a complete structure determination of the low temperature phase, the existence of strong satellite reflections at large angles and small  $k$  qualitatively indicates the presence of a displacive modulation with displacements mainly in the  $(\mathbf{a}, \mathbf{c})$  planes. Furthermore, it was recently concluded [24] from a comparison between x-ray and neutron scattering results that the vanadium atoms contributed the major part of this distortion. These results are consistent with the behavior of the high frequency dielectric constant [25], from which displacements of the V atoms in the  $\mathbf{c}$  direction have been suggested.

Although all the thermodynamic quantities extracted from x-ray scattering data (namely the order parameter, the inverse of its associated susceptibility and the correlation lengths) continuously vanish at  $T_{sp}$ , the occurrence of a slightly first-order transition is not ruled out [18]. Indeed, the measurement of a small  $\beta$  value is known to account for the small jump of the order parameter at the phase transition. In this respect, a strong coupling to lattice strains in the  $\mathbf{a}$  and  $\mathbf{c}$  directions has been measured [18], which, according to simple Landau theory can lead to a first-order phase transition. Precise synchrotron measurements will be performed to confirm this point. More puzzling is the crossover at  $\sim 50$  K in the behavior of  $T/I$ . A similar anomaly was already observed in  $\text{MEM}(\text{TCNQ})_2$  [9], where isotropic lattice fluctuations exist from  $T_c = 18$  K to 300 K, but was interpreted as due to the appearance of critical SP fluctuations locking in on a 'preexistent' soft mode, so far unexplained. Indeed, lattice fluctuations were observed even for  $T \gtrsim J$ , *i.e.* above the regime of quantum antiferromagnetic fluctuations. This is not the case for  $\alpha'$ - $\text{NaV}_2\text{O}_5$ , where the

structural fluctuations are measured for  $T \lesssim J = 280$  K. The anomaly of the thermal dependence of  $T/I$  is rather to be compared with the one observed in  $\text{CuGeO}_3$  [11]. As in this compound, it appears at the 3D-2D crossover, that we have also observed at  $\sim 50$  K.

The anisotropy ratio  $\xi_b : \xi_a : \xi_c = 3.8 : 1.8 : 1$  is similar to the one observed in the Peierls transition of the blue bronze  $\text{K}_{0.3}\text{MoO}_3$  ( $7.5 : 1.8 : 1$ ) [27], or the SP transition of  $(\text{BCP-TTF})_2\text{AsF}_6$  [9] ( $3.6 : 2.6 : 1$ ). This slight anisotropy is also to be compared with the larger one observed in the magnetic excitation spectrum by neutron scattering experiments [26] at 40 K. This indicates firstly that transverse interactions other than magnetic must be considered in order to understand the structural fluctuations. Moreover, the stabilization of the transverse components  $q_{a*} = 1/2$  and  $q_{c*} = 1/4$  requires next-nearest neighbor interactions between ladders. The long-range character of Coulomb interactions involved in the charge ordering process gives here a natural way to introduce such interactions. As far as the lattice is concerned, the coupling with the charge ordering is expected to occur through the size difference between  $\text{V}^{4+}$  and  $\text{V}^{5+}$  [22]. Nevertheless, the exact charge configuration is difficult to calculate and it has been suggested that the 'zig-zag' ordering could be stabilized *via* the lattice distortion [22]. The role of the spin gap in the stabilization of the low temperature phase could also be essential. It has been shown from symmetry reasons that in the zig-zag ordering, the existence of alternate exchange interactions responsible for the observed spin gap cannot be realized if  $q_{a*} = 0$  but only if  $q_{a*} = 1/2$ , thus coupling *via* second neighbors the charge ordering and the spin gap [22]. Seo *et al* [19] rather considered an interladder pairing for this order, *i.e.* *via* first neighbors. In both cases, the spin gap is a consequence of the transverse ordering. According to these theories, the local pairing above  $T_{sp}$  would become effective when the *transverse* correlation length  $\xi_a$  exceeds  $a$  or  $a/2$  (depending on the model considered), *i.e.* for  $T \lesssim 40$  K or 60 K. In this respect, deviation from the BF law should be visible in the 40-60 K temperature range, which can be guessed in the data published so far [12] but requires further investigations. It might also explain the anomalous behavior of  $T/I$  at  $\sim 50$  K. This is in strong contrast with the conventional SP scenario, in which the pairing becomes effective when the correlation lengths exceed the distance between spins *along* the chain [10]. From our measurements, this regime would occur below a temperature much higher than 90 K and a deviation to the BF law should have been detected. Besides, it is worth pointing out that precursor effects have been observed on the dielectric constant temperature dependence at least 8K above the phase transition [25] and on the  $C_{22}$  elastic constant variations 70 K above  $T_{sp}$  [29].

As far as the BCS-ratio is concerned, it is instructive to compare the values  $\sim 7$  [28] and  $\sim 6.5$  measured in the blue bronze and  $\alpha'\text{-NaV}_2\text{O}_5$ , respectively. In the blue bronze this deviation from the mean-field value is interpreted as being due to the existence of a strong regime

of quasi-1D structural fluctuation, depressing the phase transition temperature [28]. The same argument can be used in our case. This makes the BCS-ratio value less anomalous but raises again the question of the relation between spin gap and charge ordering, and of the nature of the transverse interactions we have shown to be essential in this new type of magneto-elastic phase transition.

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